EXPERIMENTAL AND KINETIC STUDY ON CO_2 CATALYTIC GASIFICATION OF BIOMASS CHAR USING CONVENTIONAL AND MICROWAVE HEATING

POOYA LAHIJANI AMIRI

Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

UNIVERSITI SAINS MALAYSIA

June 2014

ACKNOWLEDGMENT

In the name of God the most gracious the most merciful

First and the foremost, I thank the omnipresent God who blessed me and gave me the strength to accomplish this chapter of my life.

I would like to state my deepest appreciation to my supervisor, Professor Zainal Alimuddin Zainal for his invaluable and consistent supports and guidance. It was a pleasure and a great opportunity having the chance to work under his supervision.

I would like to sincerely thank my co-advisor, Professor Abdul Rahman Mohamed whose idea made this research possible. I will never forget his supports from the initial to the final stage of my work.

I specially want to thank my beloved wife Maedeh for her wordless encouragement and endless supports through this enduring process. She was always with me at any challenge of my life. I will always be indebted to her.

Next, I would like to express my utmost appreciation to my dearest parents for their love, patience and prayers over these years.

I would also like to thank the staff of the School of Mechanical Engineering and School of Chemical Engineering, Universiti Sains Malaysia for providing the necessary facilities to conduct this research.

Finally, I would like to acknowledge all individuals who helped me and extended their valuable assistance and generous cooperation for completion of this study.

Thank you all

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AAEM	Alkali and alkaline earth metal
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
CGSM	Changing grain size model
DTF	Drop tube furnace
EDX	Energy dispersive X-ray
FB	Fluidized bed
FTIR	Fourier transform infrared
GC	Gas chromatograph
GM	Grain model
HHV	Higher heating value
L-H	Langmuir-Hinshelwood
MH	Microwave heating
MRPM	Modified random pore model
NDM	Normal distribution function model
NMR	Nuclear magnetic resonance
PEFR	Pressurized entrained flow reactor
PID controller	Proportional-integral-derivative controller
RPM	Random pore model
S-MRPM	Shifted modified random pore model
SCM	Shrinking core model

SE	Secondary electrons
SEM	Scanning electron microscope
TB	Thermobalance
TCD	Thermal conductivity detector
TF	Tube furnace
TGA	Thermogravimetric analyzer
TH	Thermal heating
VRM	Volume reaction model
XRD	X-ray diffraction
XRF	X-ray fluorescence

LIST OF SYMBOLS

a	Time at firing (min)
A	Pre-exponential factor (min^{-1})
b	Time at 6/10 of maximum temperature (min)
c	Time to get maximum temperature (min)
c	Empirical constant in M-RPM
C_f	Free carbon active site
CO_{t_i}	Volumetric concentration of CO at time t_i (%)
C_{pW}	Specific heat of water (J/kg.K)
C_{strong}	Strong chemisorbed CO_2 (mg/g)
C_{total}	Total chemisorbed CO_2 (mg/g)
C_{weak}	Weak chemisorbed CO_2 (mg/g)
E_a	Activation energy (J/mol)
E^{app}	Apparent activation energy (J/mol)
E^{int}	Intrinsic activation energy (J/mol)
GHSV	Gas hourly space velocity (h^{-1})
I_D	Intensity of the *D* band in Raman spectroscopy
I_G	Intensity of the *G* band in Raman spectroscopy
k	Reaction rate constant
k_0	Pre-exponential factor (min^{-1})
k_1	Reaction rate constant in L-H
K_2	Equilibrium adsorption constant in L-H

K_3	Equilibrium adsorption constant in L-H
k_{GM}	Reaction rate constant of grain model (min^{-1})
k_{SCM}	Reaction rate constant of shrinking core model (min^{-1})
k_{VRM}	Reaction rate constant of volume reaction model (min^{-1})
L_0	Pore length
m	Shape factor
M_{0,CO_2}	Initial moles of CO_2 introduced to the char bed (mmol)
m_{Ash}	Mass of ash (mg)
m_{ECW}	Equivalent calorimeter mass of water (kg)
m_s	Mass of sample (kg)
m_{WC}	Mass of water in cylinder (kg)
n	Reaction order
p	Empirical constant in M-RPM
P_{CO_2}	Partial pressure of CO_2 (%)
r	Gasification reaction rate (min^{-1})
R	Specific reaction rate (min^{-1})
r_1	Temperature rate 5 min before firing (min)
r_2	Temperature rate 5 min after maximum temperature (min)
R^2	Regression coefficients
r_m	Maximum gasification rate (min^{-1})
S_0	Pore surface area (m^2/g)
t	Gasification time (min)
T_a	Temperature at firing (°C)

$\tan \delta$	Dielectric loss tangent
T_b	Temperature at b time (°C)
T_c	Maximum temperature (°C)
T_{corr}	Correction temperature (°C)
w	Instantaneous mass of the char (mg)
w_0	Initial mass of the char (mg)
W_0	Weight of dry sample (g)
W_1	Weight of sample after heating (g)
W_2	Weight of sample after heating at 750 ºC (g)
X	Char conversion (%)
X_{CO_{2},t_i}	Conversion of CO_2 at time t_i (%)
X_m	Conversion at maximum gasification rate (%)
$X(t_n)$	Char conversion at reaction time of t_n (%)
ε_0	Initial porosity of the particle
ε'	Dielectric constant
ε''	Dielectric loss
θ	Variable function
ξ	Correlation coefficient
τ_{50}	Time required to reach the conversion of 50% (min)
Ψ	Structure factor
ω	Width of the curve at $r = r_m/2$

KAJIAN EKSPERIMEN DAN KINETIK CO_2 PENGGASAN BERMANGKIN TERHADAP ARANG BIOJISIM MENGGUNAKAN PEMANASAN KONVENSIONAL DAN GELOMBANG MIKRO

ABSTRAK

Penyiasatan terhadap aspek asas proses penggasan telah menunjukan bahawa kadar penggasan arang, sebagai langkah menghadkan kadar semasa penggasan bahan karbon, memainkan peranan yang penting dalam prestasi keseluruhan penggasan. Projek ini menerokai kaedah untuk memudahkan penggasan CO_2 arang dan meningkatkan kereaktifan arang semasa tindak balas penggasan. Dalam kerja ini, kulit buah kelapa sawit (OPS) dan tempurung pistachio (PNS) telah digunakan untuk menghasilkan arang untuk penggasan CO_2. Ujikaji awal penggasan CO_2 telah dijalankan pada keadaan isoterma dalam penganalisis Termogravimetri (TGA). Pengaruh pemangkin logam pada kereaktifan penggasan CO_2 arang dikaji. Pemangkin yang digunakan adalah (a) jenis besi ($FeCl_3$, $Fe(NO_3)_3$ dan $Fe_2(SO_4)_3$) dicampur pada arang OPS, (b) logam nitrat (KNO_3, $NaNO_3$, $Ca(NO_3)_2$, Mg $(NO_3)_2$) dan $Fe(NO_3)_3$) dicampur pada arang PNS, dan (c) abu tandan kosong kelapa sawit (EFB-abu), sebagai pemangkin semula jadi yang kaya dengan kalium, dicampur pada arang OPS. Keputusan kajian penggasan bermangkin mendedahkan bahawa aktiviti pemangkin tertumpu ditumpukan kepada 5% berat $Fe(NO_3)_3$-OPS, 5% berat $NaNO_3$-PNS dan 10% berat campuran EFB-abu dan arang OPS. Beberapa model kinetik termasuk model teras mengecut (SCM), model fungsi pengedaran normal (NDM), model liang rawak (RPM) dan model liang rawak terubahsuai (MRPM) telah digunakan untuk menggambarkan kadar tindakbalas penggasan dan tenaga pengaktifan di samping menentukan parameter kinetik yang lain.